High and Low Pressure Distillation

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Introduction

Engineers and scientists frequently have the problem of separating a mixture into its components or need to purify a specific product. To solve the problem they usually apply a heuristic procedure, such as the following McMaster five-stage method:

1. Identify and define the problem.
2. Propose and develop several alternatives to solve the problem.
3. Based on available resources, choose one or two of the best alternatives.
4. Work on the chosen alternatives in greater detail and compare them before selecting the most appropriate solution.
5. Evaluate and decide if the problem has been solved.

Let us assume that, for step 1, the problem is identified as the recovery of one or more organic compounds from a mixture, or the purification of a specific chemical.

In order to apply the second step, the differences in physical properties are taken into account. Sometimes the physical properties of the components are very different, so that, if two phases already exist in the mixture, mechanical separations such as filtration or decanting may then be used. But more often the components of the mixture form a single phase and other differences in physical properties need to be found.

When a homogeneous mixture is formed with components of different vapour pressure or different boiling points, then distillation may be one of the several alternatives proposed in step 2. As will be seen later, the relative volatility (α) of a mixture is:

$$\alpha_{i,j} = \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j} \approx \frac{p_i^0}{p_j^0}\frac{\gamma_i}{\gamma_i}\frac{\phi_j}{\phi_i} \qquad [1]$$

where K_i and K_j are the equilibrium constant for components i and j respectively. These K values provide for each component a linear relationship for the mole fraction in the gas phase and the mole fraction of the same component in the liquid phase. Eqn [1] shows that the equilibrium constant and relative volatility depend on the ratios of vapour pressure, liquid-phase activity coefficients (γ) and vapour-phase fugacities (ϕ).

The relative volatility α is a measure of the ease of the separation.

- If $\alpha = 1.0$ the separation is not possible by distillation.
- If $\alpha \geq 1.2$, distillation will probably be a good alternative, and should be chosen as the next step.

In step 4, the distillation system should be designed. The design and analysis of these columns operating at high and low pressure form the core of this manuscript and are presented in the next sections.

Finally, in step 5, the scientist or engineer debates whether the problem have been solved satisfactorily. If this is the case, the problem is finished; if not, it is necessary to go back and start again.

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Distillation

Distillation is based on diffusion of one or more components through a mixture operating at a temperature, pressure and composition that assures the presence of liquid and vapour phases. In distillation, the mass transfer is due to a concentration difference moving from a place of high concentration to one of low concentration; it is not bulk movement as a result of a pressure gradient, like pumping liquid through a pipe.

Relative Volatility

The key separation factor in distillation is the relative volatility, defined by eqn [1]. As the value of relative volatility increases, the easier it is for components to be separated by distillation.

The number or theoretical stages required to separate two species to a desired degree is strongly dependent on the value of α.

The variation of this parameter with pressure is shown in **Figure 1** for the system ethane–propane. As seen, α is greater at low pressure than at high pressure. Therefore, at low pressure (e.g. 1 atm), for

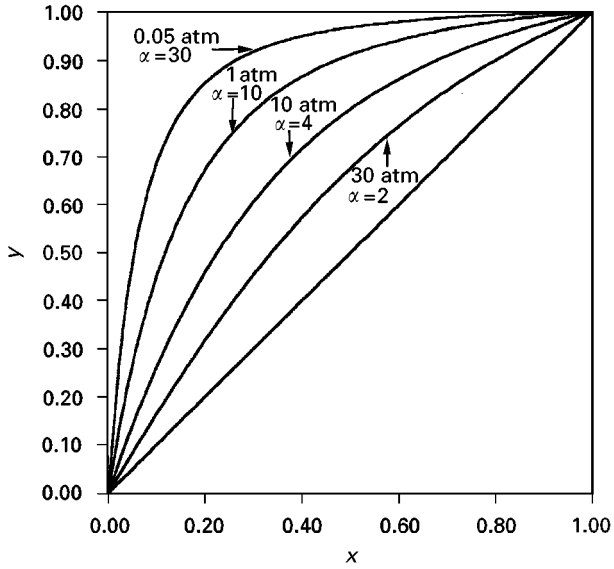

Figure 1 Variation of relative volatility with pressure.

a specified separation, the number of theoretical stages is less than at high pressure (e.g. 10 atm). In this case, why not use low pressure for this separation? As will be seen later, the temperature at the top and bottom of the column plays an important role in this decision. At low pressure (0.05 atm) top temperature $-130^{\circ}C$, while at high pressure (30 atm) top temperature is $10^{\circ}C$. Therefore, distillation at high pressure is used since it is much easier and more economical to reach $10^{\circ}C$ than $-130^{\circ}C$.

Classification, Equipment and Design of Distillation Columns

Distillation is the separation process most used in the chemical and petrochemical industry; as shown in **Table 1**, its operation is classified into several forms.

Most of the time, distillation is carried out in vertical columns or towers (like the packed column shown in **Figure 2**) where the liquid descends while the vapour ascends to the top of the column. The vapour left at the top of the tower is condensed and at least a fraction is returned back to the top of the tower as liquid reflux. Part of the liquid leaving the bottom of the column is vaporized in a reboiler and returned to the column as boil-up.

How the distillation equipment operates and how it is calculated has been modified over the years. **Figure 3** shows some developments related to distillation.

The design or sizing of distillation equipment requires the calculation of diameter and height of the column. Diameter depends on volumetric flow rates of liquid and vapour inside the column, and these are functions of the total amount of the mixture feed to the column and the reflux or boil-up ratios. The desired purity of the components at the top and bottom of the tower dictates the height of the column. First, the theoretical or ideal plates are calculated, then efficiency is estimated to convert from ideal to real stages. By specifying the distance between plates (30–60 cm), and providing space for about four plates at the top of the column and six for the bottom for disengagement of the phases, the total height of the shell is determined. **Figure 4** shows a block diagram for a typical design of a distillation column.

Distillation at high and low pressures involves special characteristics, summarized in **Table 2**.

With Internal Devices of Distillation Columns

There are three types of internal devices which provide the intimate contact between phases in a distillation column. These are tray, random packing and structured packing.

Table 1 Different classifications of distillation equipment or operation

Amount of compound to be separated	Solute recovery
	Fractionation
Mode of operation	Steady-state
	Unsteady-state
	Batch
	Semibatch
	Start and shut-down
Mixing between phases	Stagewise contact
	Continuous contact
Internal device used	None
	Plates
	Bubble cups
	Sieve
	Valve
	Packing
	Random
	Structured
System characteristics	Flash
	Fractionation
	Azeotropic
	Extractive
Operating pressure	Low
	High vacuum
	Medium vacuum
	Low vacuum
	Medium
	High

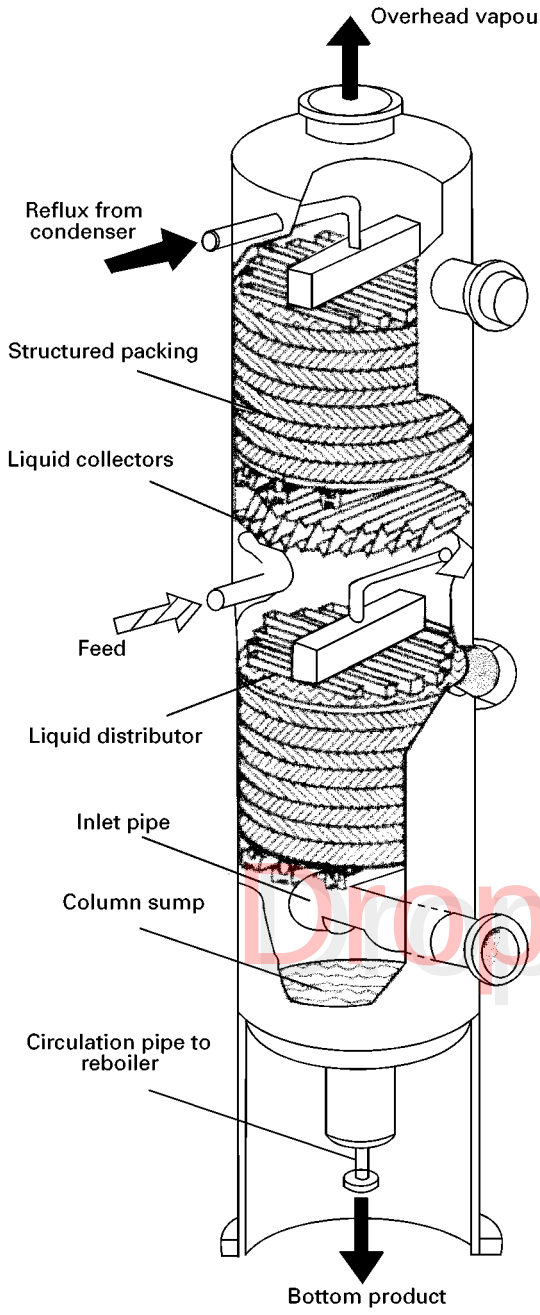

Figure 2 Distillation column equipped with structured packing.

Each has advantages and disadvantages. Trays have been used for many years. Random packings have also been used over three generations of design. Structured packings have replaced trays, especially in applications at low and atmospheric pressures. At high pressure, trays perform better than packings.

For any applcation one must determine whether tray or packing is the most appropriate. The following factors are an indication of when trays or packings are favoured.

Factors favouring trays

- High liquid rate (this occurs when high column pressures are involved);
- large diameter (packing prone to maldistribution);
- complex columns with multiple feed/take-offs;
- feed composition variation;
- scale-up less risky;
- columns equipped with tray weigh less than those equipped with some packings.

Factors favouring packings

- vacuum conditions;
- low pressure drop required;
- in smaller diameter columns (where trays are more difficult to install, diameters 0.6–0.9 m or less);
- corrosive system (more construction materials available);
- foaming;
- low liquid hold-up.

High Pressure Distillation

As seen from **Table 3**, distillation at high pressure cover a wide range of applications that have some of the following characteristics:

1. The compounds have low molecular weight (like C_2, C_3, C_4 hydrocarbons).
2. Cooling water can be used in the condenser.
3. A change in pressure could change the azeotropic point by more than 10% (in mole fraction).
4. Energy is integrated between condensers and reboilers of different columns.

Sometimes the increase in pressure is limited by the heat sensitivity of the bottom product (it could polymerize or degrade) or by its critical temperature or pressure. As is known, at the critical conditions only one phase exists. If the mixture reaches this point two phases cannot exist anymore and therefore separation is not possible. It is necessary, therefore, to be careful when one is thinking of the operating column pressure.

The upper pressure could be limited by economical conditions. If water is used as cooling medium at the top, the pressure required may be too high and therefore it would be necessary to use a refrigerant. Some authors recommend a upper pressure value of 1.48 MPa using a total condensation with water, 2.52 MPa using partial condensation with water, and if the pressure required is higher than this value it is recommended to fix the top pressure at 2.86 MPa using partial condensation with a refrigerant.

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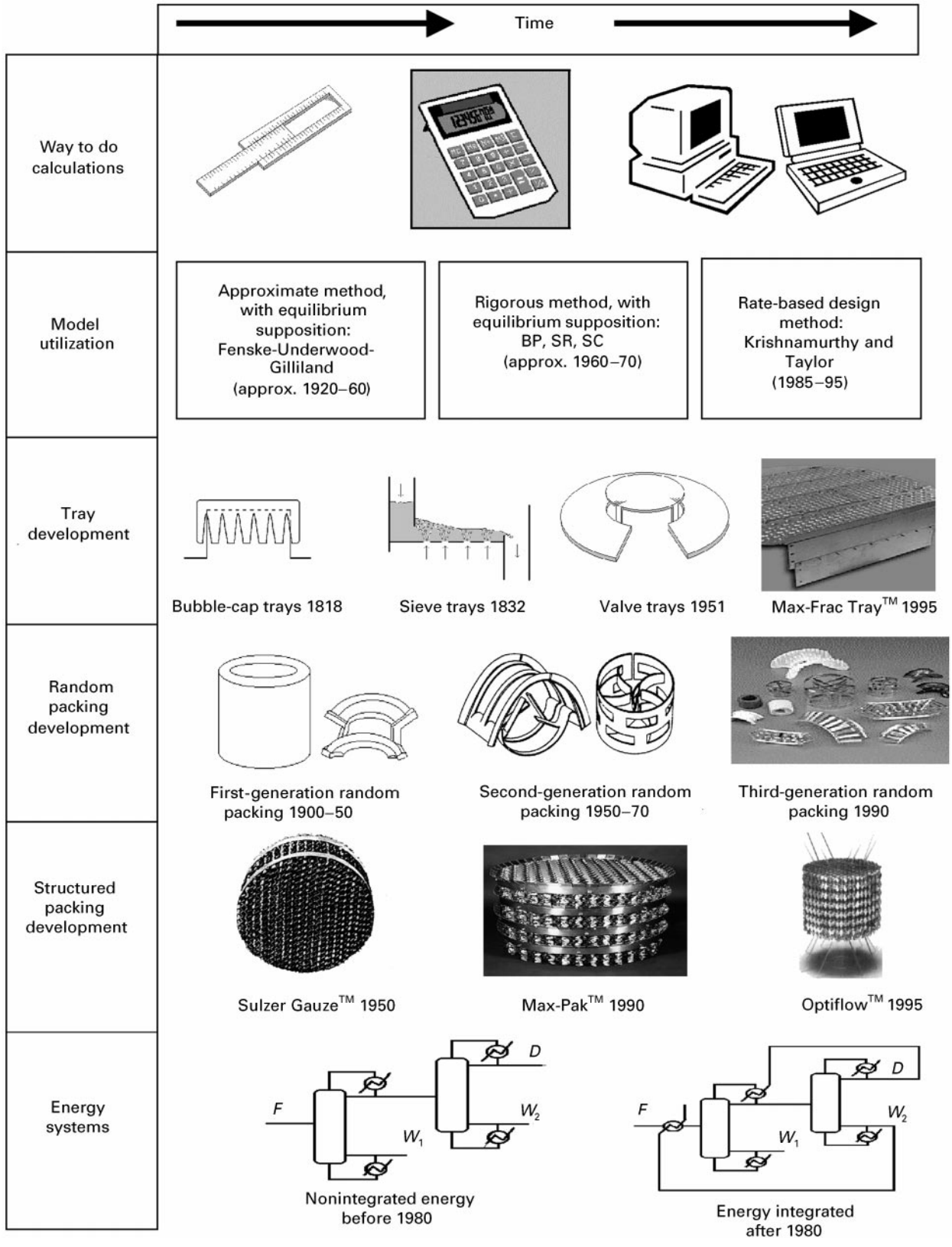

Figure 3 Paradigm shifts related to distillation. (With permission from Chemical Engineering Process (1972) 68 (8): 16).

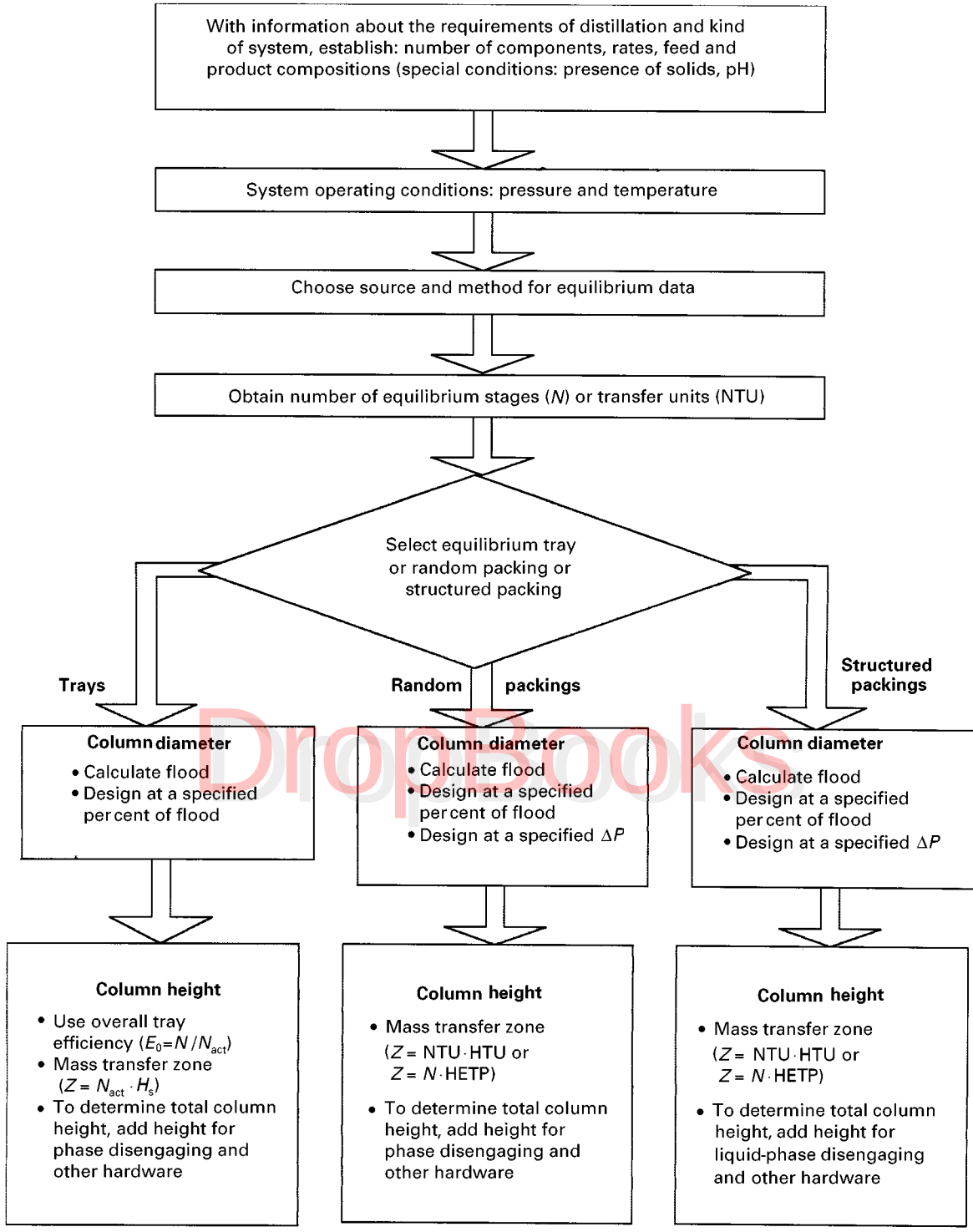
With information about the requirements of distillation and kind of system, establish: number of components, rates, feed and product compositions (special conditions: presence of solids, pH)
System operating conditions: pressure and temperature
Choose source and method for equilibrium data
Obtain number of equilibrium stages (N) or transfer units (NTU)
Select equilibrium tray or random packing or structured packing
Trays
Random packings
Structured packings
Column diameter
• Calculate flood
• Design at a specified per cent of flood
Column diameter
• Calculate flood
• Design at a specified per cent of flood
• Design at a specified ΔP
Column diameter
• Calculate flood
• Design at a specified per cent of flood
• Design at a specified ΔP
Column height
• Use overall tray efficiency ($E_0 = N/N_{act}$)
• Mass transfer zone ($Z = N_{act} \cdot H_s$)
• To determine total column height, add height for phase disengaging and other hardware
Column height
• Mass transfer zone (Z = NTU·HTU or $Z = N$·HETP)
• To determine total column height, add height for phase disengaging and other hardware
Column height
• Mass transfer zone (Z = NTU·HTU or $Z = N$·HETP)
• To determine total column height, add height for liquid-phase disengaging and other hardware

Figure 4 Procedure for designing a distillation column.

The upper pressure also could be limited by cost. If pressure is increased above 1 MPa, all equipment costs begin to go up. For instance, a stainless steel column with sieve trays could double in cost when the pressure is raised from 0.1 to 3 MPa. A similar relationship exists for other equipment and materials of construction.

Some specific applications of high pressure distillation are given in Table 3. Most applications are in the petrochemical industry, but another very important

Table 2 Characteristics of high and low distillation operation

Feature	*Low pressure*	*High pressure*
When is it used?	Products sensitive to temperature (thermal degradation)	Gas feeds ($C_2/C_3/C_4$ separation, air separation and ammonia recovery)
	Avoid using high pressure steam	Allow water to be used in the condenser
	Break azeotropes and allow separation of the system; also when a significant change occurs at the azeotropic composition (about 5%) with change in pressure	
	When trains of distillations columns with energy integration are desired allow energy of overhead vapour partially to vaporize the bottom of the other column)	
	High molecular weight of components	Low molecular weight of components
Liquid density	No significant change	Decreases slowly when pressure increases
Vapour density	Low; decreases if pressure decreases	Increases quickly if pressure increases
Liquid diffusivity	Low; increases slowly if pressure increases	Increases quickly if pressure increases
Vapour diffusivity	High; decreases if pressure increases	Low; decreases quickly if pressure increases
Liquid viscosity	High; decreases quickly if pressure increases	Low; decreases quickly if pressure increases
Vapour viscosity	High; no significant change at low or high pressure	High; no significant change at low or high pressure
Relative volatility	Increases if pressure decreases	Decreases if pressure increases
Flow parameter $F_p = \frac{L}{G}\sqrt{\frac{\rho_G}{\rho_L}}$	< 0.1	> 0.3

application is cryogenic air separation. This is based on a low and high pressure distillation column. The reboiler of the low pressure upper column (0.13 MPa) cools the condenser of the high pressure lower column (0.60 MPa). As can be seen, the high pressure column does not have a high pressure value but neither is it at atmospheric pressure.

The Further Reading section cites a good report on high pressure distillation by Brierley which gives some tips on improving an existing column and designing a new one. High pressure distillation begins about 1 MPa, where liquid density, liquid viscosity and surface tension are unusually low, while vapour density is high. Trays are recommended as internal devices, especially above 2 MPa; below this value, trays and packings must be evaluated. Many problems in high pressure distillation could be avoided with an appropriate design. Available design methods for low pressure can be applied to high pressure but with some corrections, specifically in downcomer design because this is where liquid flooding usually starts in high pressure distillation, while in low pressure, the bottleneck is the vapour flow through the active area. Downcomer design should consider both downcomer back-up and downcomer velocity.

Three flow regimes may exist in industrial columns: spray, froth and emulsion (see Further Reading). In high pressure distillation, tray operation is usually in the emulsion regime, where liquid loads are high and vapour velocities comparatively low. However, in small diameter column (less than 1.5 m) at low liquid loads or at the low end of the high pressure range (about 1 MPa), froth and spray regimes can be found. In the spray regime, flooding is caused by excessive entrainment of liquid from the active area to the tray above. It increases the tray pressure drop and the entrained liquid recirculates to the tray below. The larger liquid load in the downcomer and the increased tray pressure drop together cause the downcomer to overfill, so that the tray floods. In the emulsion

Table 3 Specific applications of high pressure distillation

Application	*Pressure Range*
Ethylene plant	
Demethanizer	32 MPa
Deethanizer	27 MPa
C-2 splitter	16 MPa
Depropanizer	19 MPa
Debutanizer	5 MPa
Dimethyl ether (DME) production (via the dehydration of methanol)	
DME column	1.60 MPa
Water column	0.75 MPa
Production of heptenes from propylene and butenes:	
$C_3 + C_3^=$/mixture separation	0.60 MPa
Miscellaneous hydrocarbons	
Propylene/pronane separation	2.1 MPa
Cryogenic air separation	
Lower column	0.6 MPa

regime, there is little entrainment of liquid by the vapour; instead, the high liquid load causes the downcomer to overfill and the tray to flood. In the froth regime, which is between the spray and the emulsion ones, flooding may be by either mechanism, depending on tray spacing and the particular combination of vapour and liquid loads.

A new model for the design or analysis of sieve tray columns has been developed at the University of Texas at Austin, in its Separation Research Program. This model applies to both low and high pressure columns. The model was adjusted with a wide experimental database from the open literature and also from the Separation Research Program facilities.

The equipment used to perform distillation at high pressure is basically the same as that used for close to atmospheric pressure, but the following special considerations should be taken into account.

1. The physical properties move in the direction indicated in Table 2 (liquid density, liquid viscosity and surface tension are low and vapour density is high).
2. The thickness of the shell and column peripheral equipment must be greater.
3. The advantage in capacity and/or efficiency of structured packing over random packing and plates decreases as the pressure increases.
4. At very high pressure the efficiency of distillation decreases, due to back-mixing.
5. At very high pressure the use of plates (standard and high capacity) is more reliable than packing.

The design equations for packed columns are basically the same, with one possible correction to the height of a transfer unit (HTU) value, to take into account the deviation from plug flow:

$$\mathrm{HTU_{total}} = \mathrm{HTU_{plug\ flow}} + \mathrm{HTU_{back\text{-}mixing}} \qquad [2]$$

Remember that at high pressure the density of gases increases by several orders of magnitude; the opposite is true for the diffusivity of the gas phase, and the surface tension decreases to very low values.

Low Pressure Distillation

Modern society is becoming ever more demanding in the quality of the products it uses and for health and environmental reasons a better removal of some components is required. This better purification of many products sometimes requires operating at very low pressure. Fortunately, the development of industrial equipment to obtain better and lower vacuum has been maintained. The cost of carrying out these operations is of course more expensive than at around atmospheric pressure. The increase in cost is inversely proportional to the absolute operating pressure.

Distillation at low pressure is used for special cases with one or more of the following characteristics:

1. heat sensitive products;
2. liquid feeds or liquid residue with high viscosity;
3. liquids with fouling and/or foaming tendencies;
4. low operating pressure (medium and high vacuum);
5. low residence time.

The applications may be classified into four groups:

- distillation or evaporation of sensitive organic chemicals;
- concentration of foods, chemicals, polymers and biological compounds;
- recovery of organic solvents;
- desolventing, devolatilization and finishing of polymer solutions.

Table 4 shows the levels of vacuum used and also lists representative equipment. Some advantages of vacuum and molecular distillation are:

- low residence time;
- high selectivity due to the higher values for relative volatility;
- cheaper heating requirements.

Some of these special kinds of distillation are discussed below.

Agitated Thin-film or Wiped-film Evaporators (WFE) and Short Path Distillation Equipment

For medium vacuum distillation, thin-film evaporators are used with or without agitation, but evaporators with scraping blades provide better performance and flexibility. Where there are heat-sensitive substances, thermal decomposition may occur during evaporation. Decomposition increases exponentially with temperature and linearly with duration of thermal load. A gentle distillation method therefore reduces the evaporation temperature and the residence times at high temperature.

Since the evaporation temperature depends on pressure, evaporation is performed under vacuum at considerably lower temperatures. If, in addition to applying vacuum, the thickness of the material on the

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Table 4 Classification of low pressure distillation

	Approximate pressure	*Typical equipment*
Low vacuum	760 to 1 Torr (1000 to 1.315789 mbar)	Vacuum column internals Plates Random packing Structured packings
Medium vacuum	1 to 10^{-3} Torr (1.315789 to 0.013157 mbar)	Thin-film evaporators Agitated thin-film evaporators
High vacuum	10^{-3} to 10^{-7} Torr (0.013157 to 0.0000013 mbar)	Short path distillation Molecular distillation Rotary stills Falling-film stills Wiped-film stills Centrifugal stills

Adapted with permission from Eckles AJ (1997) Difficult to process? Vacuum it! *Chemical Engineering* 94–100.

evaporator wall is reduced, lower evaporation temperature and shorter residence times can be achieved.

Most WFE are vertical cylinders where the feed material is distributed to the inner surface; as the liquid flows downward, axially arranged blades or roller wipers distribute the liquid as a thin film which is constantly mixed. In **Figures 5** and **6**, two types of WFE are shown. Figure 5 illustrates a WFE with rotating blades, while Figure 6 shows a unit with roller wipers and condenser. The last feature is a distinct characteristic of short path evaporators and molecular distillation stills. These types of equipment operate at the lowest pressure and provide the lowest pressure drop.

The double-walled evaporator jacket is heated continuously with a heating medium. A vacuum system (often a combination of several individual pumps) reduces the pressure in the distillation chamber.

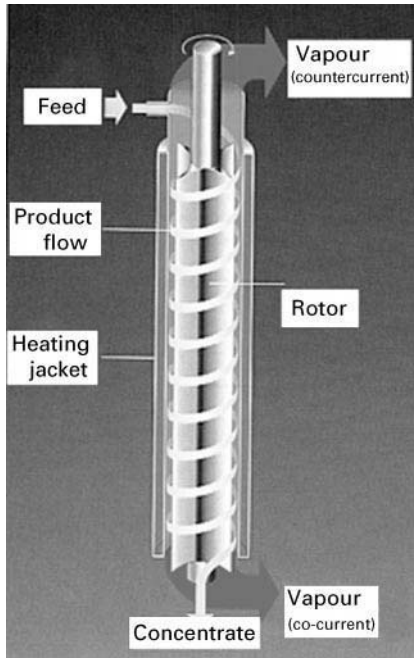

Figure 5 Agitated thin- or wiped-film evaporator (WFE) with rigid blade rotor.

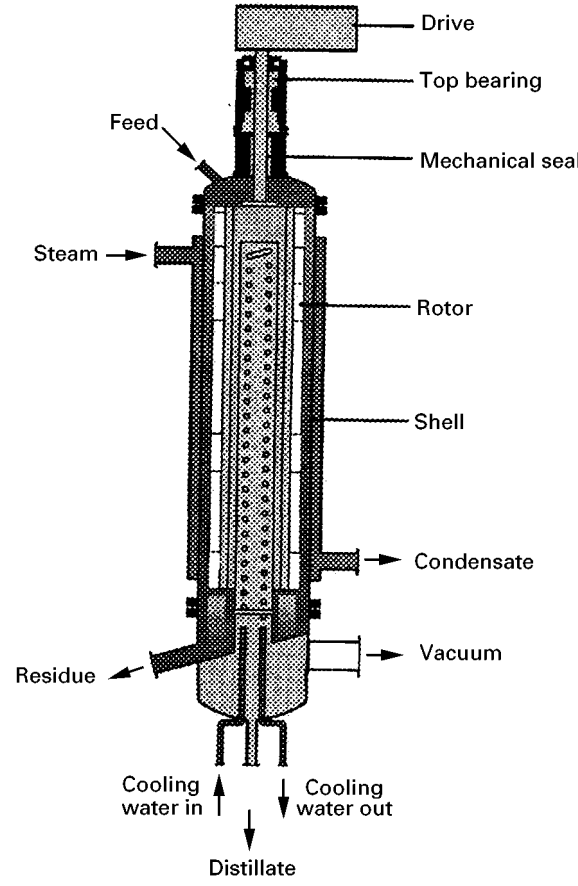

Figure 6 Wiped-film evaporator or short-path distillation equipment, with roller wiper system.

Depending on the temperature and the pressure in the distillation chamber, vapours leave through the vapour discharge and travel to an external condenser. Involatile substances are discharged at the lower end of the evaporator.

The cylindrical evaporation chamber is externally heated with hot pressurized water, steam or heat transfer oils.

Essential parts of a WFE are the rotating blades or roller wiper system, which are axially arranged in the evaporator. The blades (or roller wiper system) influence the following aspects:

- Film thickness: the components to be evaporated are more easily separated from a thin film.
- Uniformity of distribution: uniform distribution of the feed material on the evaporator surface promotes excellent heat transfer and avoids overheating.
- Mixing of the film: optimal mixing within the liquid film increases the complete separation of the components, thus enhancing evaporation.
- Residence time: if gentle distillation is required, heat-sensitive materials can be heated in the evaporator for only a short period of time. With a well-constructed blade or wiper system, the residence time can be considerably reduced.

Thin-film evaporators can be totally vacuum-sealed, thus avoiding any oxidation of product caused by penetration of air.

Discharge of the distillate vapours takes place above the feed nozzle. This is why undistilled liquid droplets, which may occur during flash evaporation, are trapped in the head of the evaporator and then flow back to the evaporator surface.

McKenna (see Further Reading) provides equations to design or analyse operation of a WFE. Some of the important equations to calculate the final concentration C_F of the residual liquid are:

$$C_F = \frac{C_0 - C^*}{(1+\alpha)^{n_{total}}} + C^* \qquad [3]$$

$$\alpha_n = 2\pi^{1.5}\mathrm{Dif}^{0.5}\frac{w^{0.5}d_e^2\tan\phi}{QN_b^{0.5}} \times\left[1+\frac{2N_bQ^{0.5}}{\pi^{2.5}d_e^2w^{0.5}\tan\phi}\left(\frac{\pi d_e}{N_b}-l_b\sin\phi\right)^{0.5}\right] \qquad [4]$$

$$n_{tot} = \frac{H_e d_e}{d_e H_s} = \frac{H_e N_b}{d_e \pi \tan\phi} \qquad [5]$$

Advantages of the process of WFE and short path distillation Thin-film evaporators offer a number of advantages. If higher operating pressure and temperature are required for economic reasons, thermally sensitive materials can still be processed because of the short residence times utilized in WFE equipment.

The thin liquid film and turbulent mixing of the film result in very quick attainment of equilibrium. This is especially important if a complete separation of a low boiling, volatile component out of the residue is required. This is why thin-film evaporators are successfully used as reboilers for rectification columns.

Thin-film evaporators are excellent degassers. If, for example, small quantities of a volatile component have to be removed down to only a few p.p.m., the evaporation capacity is not very important. The main goal in this case is to transfer the portions to be separated as completely as possible to the surface of the film. The transport is achieved by the roller wiper or blade system.

Molecular Distillation

Molecular distillation may be considered as a special version of evaporative distillation in which the liquid is evaporated without boiling, but in such circumstances that the evaporating molecules reach the condenser surface without obstruction. Three conditions for molecular distillation are:

1. Pressure must be lower than 0.001 mmHg. This low pressure is required to ensure that the molecules do not collide with each other.
2. The distance between evaporation and condensation surfaces is of the same order of magnitude as the mean free path of the molecules and the free motion of the molecule is not mechanically hindered.
3. The temperature of the condenser surface should be between 50 and 100°C lower than that of the evaporation surface to prevent re-evaporation of molecules.

The mean free path λ is given by:

$$\lambda = \frac{1}{\sqrt{2\pi\sigma^2 N}} \qquad [6]$$

where σ is the diameter of the molecule in centimetres and N is the number of molecules in 1 cm^3. By reducing the pressure to very low values, N decreases, giving values for λ of 1–3 cm, in the range of the distance between evaporator and condenser surface.

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In molecular distillation the maximum or theoretical rate of evaporation was proposed by Langmuir in 1916:

$$W_e = 0.0583 P_{mm} \sqrt{\frac{M}{T}} \quad [7]$$

where M is the molecular mass and T is the absolute temperature.

The relative volatility is given by:

$$\alpha_{1,2} = \frac{p_1^0}{p_2^0} \frac{\gamma_1}{\gamma_2} \frac{\sqrt{M_2}}{\sqrt{M_1}} \quad [8]$$

From these two equations it may be seen that molecular weight of the compounds involved is an important consideration.

Equipment for molecular distillation and medium vacuum is expensive, but it is economically justified for the separation of high value products such as vitamins, fats, essential oils and hormone concentration.

Typical unit operations and applications for medium and high vacuum using WFE, short path equipment or molecular distillation are shown in **Table 5**.

Table 5 Specific applications of low pressure distillation

Unit operations where wiped-film evaporators (WFE) are used	
Evaporation	Drying
Concentration	Degassing
Distillation	Reactions
Stripping	Deodorizing
Heating	

Distillation	*Concentration*
Application of WFE for distillation and concentration at pressure of 1–1000 mbar	
Acrylonitrile	Extract solutions
Essential oils	Insulin
Amines caprolactam	Peroxides
Quinoline derivatives	Phospholipids
Dioctyl phthalate	Pyrethrum
WFE for distillation and concentration of viscous products	
Fatty alcohols	Resins
Waxes	Honey
	Glue
	Polymers
	Lubricant oils
	Silicone fluids
WFE for distillation and concentration of products liable to encrust the heated surface	
Used oils	Contaminated effluents
Solvents containing impurities	Residue products from rectification and evaporation plants

Technologies to Improve Distillation Processes

There are several ways of improving the separation of mixtures into the desired products. Some of these combine distillation with other processes (like adsorption, stripping, pervaporation, reverse osmosis, membranes, etc.). Others are improvements to the internal devices (such as high efficiency trays or high efficiency packings). There are also the so-called enhanced distillation methods (like extractive distillation, homogeneous and heterogeneous azeotropic distillation, reactive distillation, heat integration, high gravity distillation, spinning cone distillation, mechanical vapour recompression, and pressure swing distillation). Further information about these technologies can be found in the texts cited in the Further Reading section.

Conclusion

In the 21st century, distillation at high, medium and low pressure, will continue to be a much used method for the separation of components from homogeneous mixtures.

See also: **I/Distillation. II/Distillation:** Historical Development; Theory of Distillation. **Membrane Separations:** Filtration.

Further Reading

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Historical Development

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Introduction

Distillation is one of the oldest and most widely studied unit operations in chemical engineering. It is familiar as a separation technique to chemical, process and petroleum engineers and to chemists. The common techniques, design methods and numerous applications have been extensively documented in monographs and in the journal literature (and conference proceedings) over many decades. Specialist texts and more general handbooks should be familiar to those working in related fields, therefore these standard sources are not documented here. The importance of distillation and its future directions have been discussed by Kunesh *et al.* (1995) and by Porter (1995) (see Further Reading). This article presents a state-of-the-art overview of distillation by concentrating on recent advances and possible future developments.

Sources of Information and Data

For a subject as old as distillation, and with such a wide range of applications, there is an extensive collection of published information. With the advent of electronic databases and online web-based resources it has become much easier to perform literature searches on particular topics and to keep abreast of the current literature and recent developments. For this reason an extensive reference list to journal articles is not provided in the Further Reading at the end of this article. Selected papers are included that can be used to locate related references. Author or subject searches of the journal literature (from 1956 to the present, with six-monthly updates) can easily be performed by using the **CHERUB**™ *Chemical Engineering Database* (complied by M. S. Ray) which is included on the *Engineering & Applied Science CD-Rom Database*. The ability to easily search the chemical engineering literature is a recent development, and is an important advantage for distillation researchers. Another useful reference source is a series of annual update bibliographic papers on 'Equilibrium-staged Separations' (e.g. *Separation Science and Technology* 32(18): 3067–3083, 1997). Patent searches can also be performed on the web, e.g. *www.ibm.com/patents*, and *www.uspto.gov* (the website of the US Patent & Trademark Office). Several handbooks and monographs (and CD-ROMs) containing property data useful for distillation systems have also been compiled, e.g. C. L. Yaws (transport properties data and thermodynamic diagrams); J. Gmehling and co-workers (including VLE data, heats of mixing, azeotropic data); and the *American Institute of Chemical Engineers*' Design Institute for Physical Property Data (*DIPPR*) publications.

Prediction of Vapour–Liquid Equilibria (VLE) Data

Significant advances in the interpretation and prediction of vapour–liquid equilibria (VLE) data have been made since the 1970s. These advances developed from the publication of a range of equations of state (EOS) based upon the application of traditional thermodynamic principles and relationships. The EOSs provide interpretation or evaluation of available experimental VLE data. The Wilson model (1964) is probably the most popular for dealing with liquid-phase activity coefficients because it has only two adjustable parameters, and it works well for both binary and multicomponent systems. The prediction of nonidealities in binary mixtures using the UNIQUAC model (1975) is rather more complex. Subsequent and related studies led to the development and use of the Group Contribution Methods such as ASOG and UNIFAC for the prediction of VLE data. The latter is widely used when actual system data are not available, provided that an approximate nonideality correction is acceptable. New methods are being developed and probably the one showing most promise and of general applicability is known as: A Generalized Approach to Phase Equilibria (AGAPE, 1995).

There are many EOS models described in the literature but only a few have wide use for engineering

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